

Combined Sr and Cs exchange in a natural clinoptilolite

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Introduction

The natural zeolite, clinoptilolite, $(\text{Na,K})_6\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 20\text{H}_2\text{O}$, is useful in industry for its cation exchange capabilities. Because of its selectivity for certain cations, clinoptilolite has been used for the removal of Cs and Sr from low-level radioactive waste solutions. Since its opening in 1985, British Nuclear Fuels' Site Ion Exchange Effluent Plant (SIXEP) has been responsible for the removal of ⁹⁰Sr and ^{134,137}Cs from radioactive cooling-pond waters by use of clinoptilolite filtering beds. The clinoptilolite does not achieve full exchange with Sr and Cs before Sr breakthrough occurs (Sr stops exchanging with the clinoptilolite), making Sr the limiting factor in the life of the exchange beds.

Experimental design

A clinoptilolite-rich rock from the Mud Hills formation near Barstow, California was used in this study to determine the exchange behavior of clinoptilolite in the presence of varying concentrations of a mixture of Sr and Cs at varying temperatures and times. Twenty samples were generated by placing 4 g of clinoptilolite in contact with 100 mL of 0.01 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.01 M CsCl. An additional 20 samples were generated by placing 4 g of clinoptilolite in contact with 0.001 M $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.001 M CsCl. Samples were then treated at 5, 21, 50, and 90°C for 0.5, 5, 24, 240, and 720 h. Samples were vacuum-filtered to remove solids. Twenty DI samples were also created by adding 4 g of clinoptilolite to 100 mL deionized water and storing them for the same period of time and at the same temperatures. Sample solutions were analyzed for the outgoing cations Na^+ , K^+ , Mg^{2+} , and Ca^{2+} and for remaining Sr^{2+} by ICP-AES. Solutions were also analyzed by AAS for the remaining Cs^+ .

Results and conclusions

Significant concentrations of Na and K are removed from the mineral in the DI samples, and to greater extents with time and temperature. In the 0.01 and 0.001 M samples, monovalent cations leave the mineral to greater extents with time and temperature, whereas divalent cations leave the mineral to greater extents with decreasing temperature. None of the outgoing cations occur in the solutions in concentrations as high as are available in 4 g of clinoptilolite. However, within 720 h of treatment, approximately all of the Sr and Cs in the original solutions is either absorbed into or adsorbed onto the mineral. Clinoptilolite exhibits a selectivity for Cs over Sr. Overall exchange of cations increases with increasing time and temperature.

Isotope ratio measurements on transient signals by an online coupled HPLC-MC-ICP-MS system

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Introduction

Coupling of sample introduction devices necessary for chemical speciation (Krupp et al., 2001), sample preconcentration (Evans et al., 2001), separation of the sample matrix or removing of interferences (Röllin et al., 1996) leads to transient signals, often of short duration. However, the best precision for isotope ratios is obtained using steady-state signals of several minutes or longer.

The objective of the study was to determine the precision and accuracy of isotope ratios on transient signals which are achieved by online coupling of a high performance liquid chromatography (HPLC) to a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS).

Experimental

A Dionex HPLC system (GS50, 25 μ l injection loop, 0.25 ml/min flow rate) was connected to the MC-ICP-MS "Neptune" (ThermoFinnigan). Since the MC-ICP-MS at the Paul Scherrer Institut will be mainly used for the characterisation of nuclear fuel samples the study was restricted to transient signals of U (main component in nuclear fuels) and Nd (burn-up monitor). Samples containing U or Nd in different concentrations were injected via a Rheodyne valve and eluted with 1 M HCl or with a gradient of α -hydroxyisobutyric acid, respectively. Typical transient signals for both elements last about 30 to 60 s.

Results and discussion

The precision and accuracy of the U and Nd measurements as a function of the elemental concentration and the integration time will be presented in comparison with results achieved on steady-state signals of the same intensity for both elements. The discussion of the results will be focussed on the question if the simplification of the sample preparation procedure (especially for nuclear materials: high risk of contamination, high dose rate for the operator) obtained by the coupling is offset by a reduction in precision resulting from measurements of short transient signals.

References

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